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METHOD FOR FABRICATION OF ELECTRODES

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METHOD FOR FABRICATION OF ELECTRODES

[0001] The United States Government has rights in this invention pursuant to Contract No. W-7405-ENG-46 between the United States Department of Energy and the University of California for the operation of Lawrence Livermore National Laboratory.

RELATED APPLICATIONS

[0002] This application is a Divisional of Serial No. 09/906,913 filed July 16, 2001 entitled "Method for Fabrication of Electrodes" by inventor(s) Alan F. Jankowski, Jeffrey D. Morse and Randy Barksdale.

BACKGROUND OF THE INVENTION

[0003] The simplest fuel cell comprises two electrodes separated by an electrolyte. The electrodes are electrically connected through an external circuit, with a resistive load lying in between them. Solid polymer electrochemical fuel cells generally employ a membrane electrode assembly, or "MEA," comprising a solid polymer electrolyte membrane, or "PEM," also known as a proton exchange membrane, disposed between the two electrodes. The electrodes are formed from porous, electrically conductive sheet material, typically carbon fiber paper or cloth, that allows gas diffusion. The PEM readily permits the movement of protons between the electrodes, but is relatively impermeable to gas. It is also a poor electronic conductor, and thereby prevents internal shorting of the cell.

[0004] A fuel gas is supplied to one electrode, the anode, where it is oxidized to produce protons and free electrons. The production of free electrons creates an electrical potential, or voltage, at the anode. The protons migrate through the PEM to the other electrode, the positively charged cathode. A reducing agent is supplied to the cathode, where it reacts with the protons that have passed through the PEM and the free electrons

that have flowed through the external circuit to form a reactant product. The MEA includes a catalyst, typically platinum-based, at each interface between the PEM and the respective electrodes to induce the desired electrochemical reaction.

[0005] In one common embodiment of the fuel cell, hydrogen gas is the fuel and oxygen is the oxidizing agent. The hydrogen is oxidized at the anode to form H^+ ions, or protons, and electrons, in accordance with the chemical equation:

$$H_2 = 2H^+ + 2e^-$$

[0006] The H^+ ions traverse the PEM to the cathode, where they are reduced by oxygen and the free electrons from the external circuit, to form water. The foregoing reaction is expressed by the chemical equation:

$$\frac{1}{2}O_2 + 2H^+ + 2e^- = H_2O$$

[0007] Solid Oxide Fuel cells (SOFCs) operate using a mechanism similar to PEMs. The main difference is that instead of the electrolyte material comprising a polymer material capable of exchanging protons, the electrolyte material comprises a ceramic material capable of exchanging electrons.

[0008] Electrode layers must be porous in order to allow the fuel and oxidant to flow to the electrode-electrolyte interfaces. Typical fuel cells that use porous electrode materials are bulk structures that require significant manifolding and pressures to readily deliver the fuel to the electrode-electrolyte interface. These porous electrodes are formed by pressing and sintering metal powders to promote adhesion, then sandwiching two such electrodes around an electrolyte layer to form a fuel cell or in series to form the fuel cell stack. A method to fabricate porous electrodes that can reduce or remove the need for high temperatures or high pressures to assist the flow of the fuel and oxidant to the electrode-electrolyte interface may be an important contribution to fuel cell technology.

SUMMARY OF THE INVENTION

[0009] Aspects of the invention include a method comprising the steps of

[0010] Simultaneously: (1) coating a topside of a porous host structure with a plurality of conductive material particles and (2) flowing gas through a bottom side of the porous host structure to form a conductive porous electrode layer on the topside.

[0011] Other aspects of the invention include an electrode comprising a conductive material having a plurality of pores, the electrode having a pore size distribution wherein at least 90% of the total pore volume is in pores of diameter from about 10% below the mode pore diameter to about 10% above the mode pore diameter.

[0012] A fuel cell comprising at least one electrode comprising a conductive material having a plurality of pores, the electrode having a pore size distribution wherein at least 90% of the total pore volume is in pores of diameter from about 10% below the size of the mode pore diameter to about 10% above the size of the mode pore diameter.

[0013] A fuel cell stack comprising at least one fuel cell having at least one electrode comprising a conductive material having a plurality of pores, the electrode having a pore size distribution wherein at least 90% of the total pore volume is in pores of diameter from about 10% below the size of the mode pore diameter to about 10% above the size of the mode pore diameter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The accompanying drawings, which are incorporated into and form a part of the disclosure, are as follows:

Figure 1 is an illustration of an electrode-electrolyte-electrode portion of a fuel formed on a host structure that has been mounted to a template;

Figure 2 is an illustration of the simultaneous processes of vacuum deposition and gas flow that form a metal electrode;

Figure 3 is an illustration of how a layer of metal greater in thickness than the diameter of the pore size of a porous host structure can be formed;

Figure 4 is an illustration of how the pore is pinched off when forming an electrode after a desired thickness of deposited metal has been achieved;

Figure 5 is an illustration of a metal electrode formed by mounting a porous template to the porous host structure.

DETAILED DESCRIPTION

[0015] Fuel cells include, but are not limited to, an anode layer, an electrolyte layer, a cathode layer and optionally catalysts to enhance reaction kinetics. Fuel cell

stacks comprise two or more fuel cells connected either in series or in parallel. It is desirable to have porous electrodes so that the fuel and oxidant can easily flow to the respective electrode-electrolyte interface without the need for high temperatures or high pressures to assist the flow. Described herein is a method to form a porous thin-film electrode structure. This approach can be used for all fuel cell electrolyte materials that utilize a continuous electrolyte layer. Moreover, the method can be used to fabricate porous electrodes useful in fuel cells such as, a solid oxide fuel cell (SOFC) and a proton exchange membrane fuel cell (PEMFC) sometimes referred to as a solid polymer fuel cell (SPFC). Power densities measured in output per unit area may be achieved up to about 1 W/cm^2 for PEMFCs and up to about 2 W/cm^2 for SOFCs. Typically power densities range from about 0.1 W/cm^2 to about 0.4 W/cm^2. The power output of these fuel cells ranges from about 0.1 Watts to about 50 Watts. Typical outputs range from about 1 Watt to about 10 Watts.

[0016] A porous thin-film anode or cathode structure may be formed from a host structure or substrate having a high percentage of continuous open porosity, e.g., greater than 40% by volume (measured by mercury porosimetry). Examples of such substrates include anodized alumina, silicon that has been anisotropically etched, or a polycarbonate film that has been irradiated by heavy ions and selectively etched by potassium hydroxide. The pore sizes in such a structure nominally range from about 0.05μm to about 1μm in average cross-sectional diameter (measured by scanning electron microscopy or optical microscopy), are closely spaced, and are continuous throughout the substrate/host structure.

[0017] Vacuum deposition techniques may be utilized to coat the surface of the host structure with conductive metals, polymers and/or ceramic materials to form the electrode. Some examples of electrode materials include silver, nickel, platinum, and lanthanum-strontium-maganate. Under appropriate process conditions, such a conductive material can be deposited to a thickness where the pores are not completely closed at the top surface of the conductive coating. Subsequent deposition and/or application of a continuous electrolyte layer, and a complimentary porous electrode can complete the fuel cell structure. If the newly deposited electrode on the porous host structure closes off the pores completely, then diffusion of fuel and oxidant through the electrode and electrolyte

layers will no longer be possible. The use of conventional vapor deposition techniques necessarily limits the thickness of the deposited electrode to a width on the order of the size of the diameter of the pores of the host structure. The electrode can have an excessively high overall electrical resistance as a consequence of such small dimensions. The resistance of the electrode can be reduced to suitable levels for efficient conduction of current when a conductive film much thicker than the diameter of the pores of the host structure can be deposited onto the host structure.

[0018] The thickness of the porous and conductive electrode can be increased when a gaseous material, such as an inert gas, e.g., Argon, at about 0.1sccm (standard square centimeters per minute) to about 300 sccm, is flowed through the pores of the host structure from the bottomside during the vacuum deposition process. The deposition rate and additional process conditions for the conductive material enable application of an electrode layer that can be constructed to be much thicker in size than the average cross-sectional diameter of the pores of the host structure, thereby significantly reducing the resistance of the electrode. For example, the poor performance that can result from high current, breakdown voltage, resistive losses in thin (less than about 0.1 μm) metals are eliminated for conductive layers greater than about .15μm in thickness.

[0019] In addition, electrodes having uniform pore size distributions from about 0.1 μm to about 10 μm wherein at least 90% of the total pore volume is in pores of diameter from about 10% below the mode pore diameter to about 10% above the mode pore diameter can be obtained. Mode pore diameter is defined as the pore diameter occurring most frequently in any given porous electrode. Tapered pores can also be obtained with this method wherein the size of the two pore openings can be tailored to specific sizes. A tapered pore is a pore with the size of one opening smaller than the size of the other opening. The sizes of the two openings can vary by up to a factor of 10. Features such as pore size and operating temperature will determine the rate at which fuel and oxidant can be passed through the fuel cell. For example, smaller pore sizes can be desirable in a low temperature PEM cell that generates up to about 0.1 watts/cm^2, whereas larger pore sizes can be desirable in a high temperature SOFC that generates up to about 2 watts/cm^2. Thus, the ability to tailor the pore size of electrodes to operating temperatures and other parameters of fuel cells can create very efficient energy systems.

[0020] Referring to Figure 1, a continuous electrolyte layer **2** is positioned between two porous electrodes, such as anode **4A** and cathode **4B**, forming an electrode-electrolyte-electrode portion of a fuel cell or fuel cell stack. Anode and cathode positions can be interchangeable. One embodiment of the method includes a porous host structure **6** having a high density of pores **7** already formed in it. In a further embodiment, host structure **6** may be mounted to a porous template **8**. Pore sizes in host structure **6** are typically between about .05μm and about 1μm, calculated as average cross-sectional diameter, whereas pore sizes in template **8** are larger than those of host structure **6**, e.g., having average cross-sectional diameters on the order of about 0.1μm to about 3μm. The direction of fuel flow through the fuel cell as shown by arrows **10**, is through pores **7** toward the electrode-electrolyte-electrode interface **5**.

[0021] Furthermore, electrolyte layer **2** is an insulating material that is ion-conducting or proton conducting. Formation of electrolyte layer **2** can be accomplished by using a physical or chemical vapor deposition method and/or a laminate method. Examples of effective methods include sol-gel, plasma spray, dip coating, tape casting, and evaporation.

[0022] Referring to Figure 2, the manner in which the conductive layer is formed is illustrated. Arrows **12** show the direction of gas flow through pores **7**. As conductive particles **14** are deposited by vacuum deposition techniques, the gas flow through pores **7** causes a plurality of conductive particles **14** to disperse away from pores **7**. The direction of vacuum deposition is shown by arrow **16**. Figure 3 is an illustration of the formation of electrode **4A** obtained from the deposition of scattered conductive particles **14** on host structure **6** (the direction of gas flow is shown by arrows **12** and the direction of vacuum deposition is shown by arrows **16**).

[0023] Another embodiment of the method for depositing the electrode is illustrated in Figure 4. After an electrode **18** of a desired thickness **19** has been deposited on host structure **6**, the rate of gas flow **12** through pores **7** is reduced in order to allow a plurality of sputter deposited conductive particles **14** to narrow down or partially pinch off pores **7** at an orifice distal to host structure **6**, i.e., to reduce the orifice dimensions of pores **7** in order to create tapered pores **20**.

[0024] Another embodiment of the method of the invention is illustrated in Figure 5. Porous host structure **6** is mounted on template **8** wherein template **8** has a grid of pores **22** larger in average cross-sectional diameter than that of the pore sizes of host structure **6**. Gas flow **12** is prevented from flowing through the pores of host structure **6** because the pores are blocked by grid **22**. If the ratio of the area of the blocked pores to unblocked pores is small, the vacuum deposition rate is greater on the surface above grid **22** resulting in an electrode **4** having a thicker layer of conductive particles at such areas **24**. The grid pattern is translated to areas of thicker electrode material on a surface having low resistance for conducting current efficiently away from the areas of porous electrode.

[0025] While particular operational sequences, materials, temperatures, parameters, and particular embodiments have been described and or illustrated, such are not intended to be limiting. Modifications and changes may become apparent to those skilled in the art, and it is intended that the invention be limited only by the scope of the appended claims.